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EVALUATION OF MECHANICAL PROPERTIES AND WEAR RESISTANT OF ELECTRODEPOSITED COMPOSITE COATINGS WITH NANO-SIZE PARTICLES

STANOVENÍ MECHANICKÝCH VLASTNOSTÍ A ODOLNOSTI PROTI OPOTŘEBENÍ ELEKTROCHEMICKY VYLUČOVANÝCH KOMPOZITNÍCH POVLAKŮ S NANOČÁSTICEMI

Abstract

This paper is a study of the electrodeposition possibilities of coatings and evaluation its mechanical properties. The composite layers on a base of Ni with contents of SiO_2, Al_2O_3, SiC, TiCN were electrodeposited. The composite coatings have been deposited in the bath containing 5, 10, 20 and 50 g of the powder in 1 dm^3 of the electrolyte. For comparison the Ni layer was also obtained and investigated in the same manner. The layers were deposited in current density range of 0,5 to 7 $A.dm^{-2}$.The microhardness of the deposited layers was measured using Vickers method at a load 0,1 kg. In order to determinate wear resistant the coatings was tested using the technique based on measuring system comprising a flat surface and ball. On the basis of the wear traces and measurement of their diameter, the depth of the wear was calculated, which was taken as a measure of wear. For mechanical properties evaluation a small punch test technique has been chosen. The state of the art of SP technology now enables to obtain mechanical properties like yield stress, strength, elongation, transition temeperature, fracture toughness, fatigue as well as creep properties of materials.

Abstrakt

Článek studuje možnosti vylučování galvanických povlaků se zabudovanými nanočásticemi a hodnocením jejich vlastností.. Byly vylučovány galvanické kompozitní povlaky s nanoprášky: SiO_2, Al_2O_3, SiC, TiCN a jejich obsah v elektrolytu byl měněn v rozmezí – 5, 10, 20 a 50 $g.dm^{-3}$. Všechny vrstvy byly vyloučeny v rozsahu katodických proudových hustot 0,5; 1, 3, 5 a 7 $A.dm^{-2}$. Pro celkové srovnání mechanických vlastností byly vyloučeny také vzorky čistého Ni. Mikrotvrdost povlaků byla hodnocena metodou dle Vickerse při zatížení 0,1 kg. Odolnost povlaku proti opotřebení (adhezivní opotřebení) byla zkoušena přístrojem “Kulotester”. Pro hodnocení mechanických vlastností byla využita metoda malých vzorků (penetrační test). Současný stav poznání u metody malých vzorků umožňuje získat hodnoty mechanických vlastností jako jsou mez kluzu a pevnost, lomová houževnatost, únavové vlastnosti a creepové vlastnosti materiálu.

1 INTRODUCTION

Protection of surface of machine or other components against influence of chemical or mechanical effects belongs to the topical problems of durability increase. Research and investigations have reached remarkable success already. First of all electrodeposited composite coatings appear as a significant step forward especially owing to wear properties of those products.

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More prospective is the category of electrodeposited composite coatings (ECC). As always at composites a combination of properties of different types of materials is utilized.

The properties of electrodeposited composite coatings (ECC) are predestinated by the both components – the matrix material and the scattered small particles. One component is the matrix. Electrodeposite metallic matrix has a good conductivity, both electric and thermal, is ductile, ferromagnetic. On the other hand the dispersed phase, either small particles, or fibres, have other advantages in a comparison to metallic matrix.. In the case of fibres high tenacity of some such materials, like carbon, boron, can be imposed, if the fibres are spooled during the electrodeposition. It means that rotational shapes can be produced only. This process is difficult, of course, for the requirement to quill filaments very slowly. The second group, the most common one, is characterized by very high hardness, or sliding properties. The share of embedded particles and their adhesion to the matrix phase are important for the final property of ECC [3]. However, the nature of dispersed particles is decisive first of all and the right choice of it is always the first step before the process investigations. The choice depends on the requested properties of the ECC, of course. The particles may be of inorganic or organic character. The first group can be divided into conductive or non-conductive materials, the latter are mostly plastics. A lot of various oxides (aluminium, titanium, chromium etc.), carbides (tungsten, vanadium, chromium, silicium, zirconium etc.) some borides have been suggested and investigated [1,2]. Molybdenum and tungsten sulphides have been used too, owing to their excellent sliding properties. Chemical resistance of these substances to the electrolyte for electrodeposition is an unavoidable requirement.

Basically all electrodeposition processes producing sound thick low stressed layers could be used. However, some of them are not suitable for mechanical properties – first of all poor hardness connected with low strength. Zinc and copper belong to those, though the latter has been investigated for this purpose too. Chromium, which is known as a very hard coating, cannot be used for very low cathodic current efficiency (less than 20%), typical for electrodeposition from hexavalent-chromium compounds, accompanied by a violent hydrogen evolution is an obstacle to dispersed particles adsorption and entrapment. Some attempts to use trivalent-chromium baths has been made, however without any obvious success. Therefore, it seems that the iron-group metals remain the most advanced matrix. If the most proper one from the three individual metals should be found, iron is the less expensive one. However, the cation Fe^{2+} tends to oxidation even by air oxygen, as mentioned in the foregoing paragraph. The trivalent iron compounds complify the electrodeposition for an extreme internal stress increase, which occurs for the presence of basic unsoluble salts and their adsorption at the cathode surface. The internal stress may be as high as to cause distortion or even crash of the deposit. Deposition at high temperatures can lead to sound deposits, but the process is rather troublesome for the risk of strong corrosion of the equipment caused by strong acid electrolyte at the mentioned temperature. Cobalt would be more proper as the electrodeposition of it does not bring troubles like iron. However, the high price of cobalt may be a limitation of its use. Of course, binary alloys, based on nickel, are of great importance, giving broader variety in properties. Not only the other iron group partners can be considered, but some other alloying elements too. If good mechanical properties at elevated temperatures (more than 250°C) are desirable, phosphorus or tungsten are recommendable.

Electrodeposited composite coatings have used fine dispersed particles of size above 1 μm till now. However, the progress which occurred in the field of very fine loose materials enables to produce and manipulate materials having grain size on the level of 10 nm. It can lead to a further increase of quality of the electrodeposited protective coatings The solution brings new questions different to the processes using bigger particles. The stability of electrolyte, i.e. lowering of velocity of sedimentation, increases – electrolyte is virtually passing to colloidal systems. The possible electric charge carried by the tiny particles may play an important role. Therefore, these typ of process can be very different to the process using bigger particles.

2 EXPERIMENTAL PROCEDURE

Copper test coupons with exposed area of 9 cm^2 were used as substrates while nickel was used as the anode. The copper coupons were degreased and decontaminated. A typical nickel sulfamate electrolyte has been used for electrodeposition of coating. The composition of nickel plating bath was*:* Ni^{2+}= 1,78 mol/l, H_3BO_3= 0,49 mol/l, Br^-= 0,1 mol/l. Experiments were conducted in 0,5 liter beakers (Fig. 1). Electrode positions were carefully maintained and solution was mechanically stirred (200 rpm and 400 rpm). A several types of dispersion phase have been used for electrodeposition of composite coating.

Fig.1 Workplace of electrodeposition ion test

The dispersion phases:

Silicon dioxide - SiO_2
- particle size: 15 nm

Aluminum oxide - Al_2O_3
- description: sigma phase
- particle size: 40-47 nm

Silicon carbide – SiC
- particle size: 45-55 nm (spheres)
- density: 3,22 g/mL at 25°C
- bulk density: 0,069 g/cm^3

Titanium carbonitride - TiCN
- avg. particle size: 50-80 nm (spherical)
- density: 5,02 g/mL at 25°C

Parameters of process:

temperature: 50°C, pH value: 3,9 - 4,1; stearing: mechanically; thickness of coating: about 100 μm for microhardness measurements and wear resistance evaluation and about 0,5 mm for mechanical properties evaluation; cathodic current density: 0,5; 1; 3; 5; 7 $A.dm^{-2}$

After each experiment the test specimens were manufactured from coupons and mounted in epoxy polymer then grinded and polished for microhardness measurement or prepare for punch test and tensile test.

3 EVALUATION OF MECHANICAL PROPERTIES

Hardness measurements were performed by the Vickers method. The method is based on hobbing of a diamond pyramide inside the maesured metal. Hardness is determined from the length of the slant of the dinge. As the thickness of electrodeposits is often rather small, the results might be affected by the base. Hence a microhardness method was used. The microhardness of the deposited layers was measured using Vickers method at a load 0,1 kg

In order to determinate wear resistant the coatings was tested using the technique based on measuring system comprising a flat surface and ball (KULOTESTER – Fig. 2). On the basis of the wear traces and measurement of their diameter (Fig. 3), the depth of the wear was calculated, which was taken as a measure of wear.

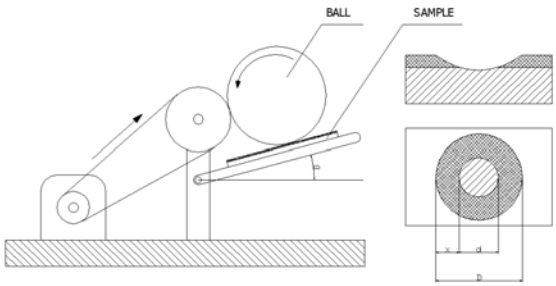

Fig. 2 Scheme of Kulotester

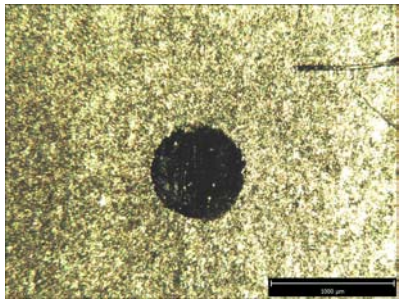

Fig. 3 Trace of wear from Kulotester (TiCN, 50g.dm^{-3}, j_k = 3Adm^{-2}, three cycles – 6000 spindle speed)

For mechanical properties evaluation a small punch test technique has been chosen.The Small Punch (SP) miniaturised test technique is a potent method capable of providing direct values for mechanical properties of materials. The state of the art of SP technology now enables to obtain mechanical properties like yield stress, strength, elongation, transition temeperature, fracture toughness, fatigue as well as creep properties of materiale [4]. The SP testing technique utilises a small disc specimen, 8 mm in diameter and 0,5 mm in thickness , clamped around its circumference and indented by a spherical punch up to failure (Fig. 5). The support at the border region of the disc may be loose, or rigid clamping. Monotonic load vs. displacement records are used to derive estimates of tensile and fracture toughness parameters (Fig. 4).

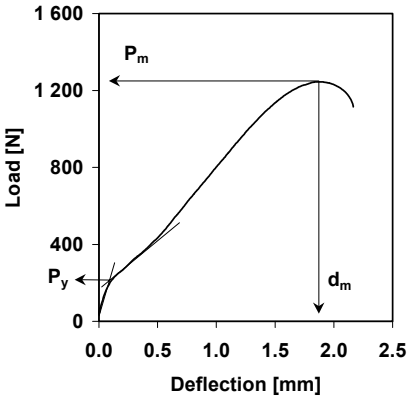

Fig. 4 Record of penetration test

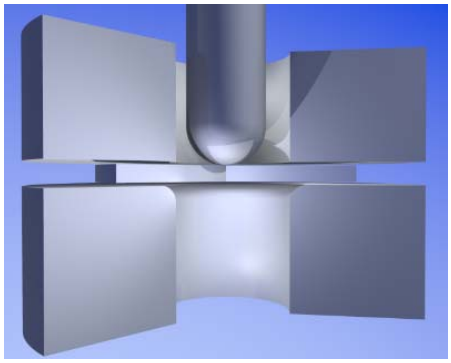

Fig. 5 Schematic drawing of penetration test

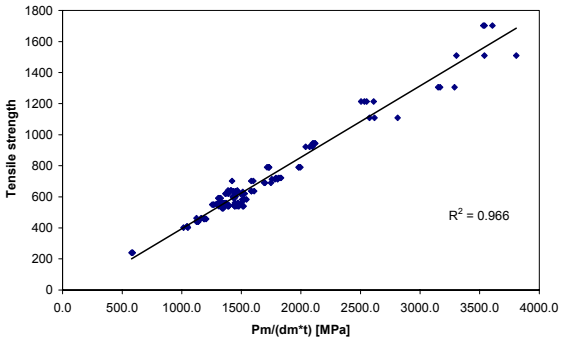

Fig. 6 Correlation between result of penetration test and tensile strength
Pm – maximum load during small punch test
dm – deflection corresponding to a maximum load

4 RESULTS AND DISCUSSION

4.1 Microhardness

The results of measurements microhardness HV 0,1 are presented in Fig. 7 – 9.

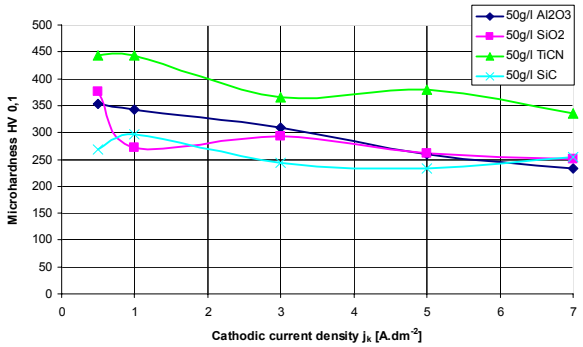

Fig. 7 Dependence of microhardness HV 0,1 on the cathodic current density

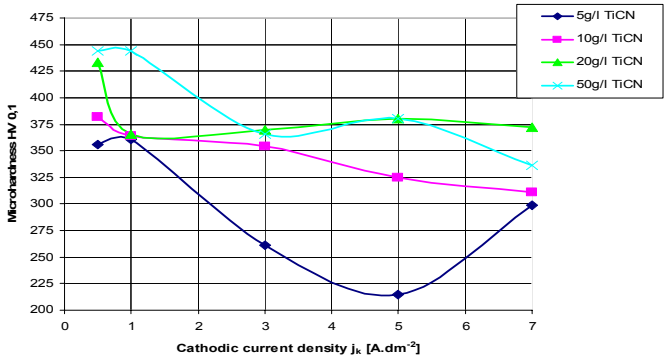

Fig. 8 Dependence of microhardness HV 0,1 on the cathodic current density

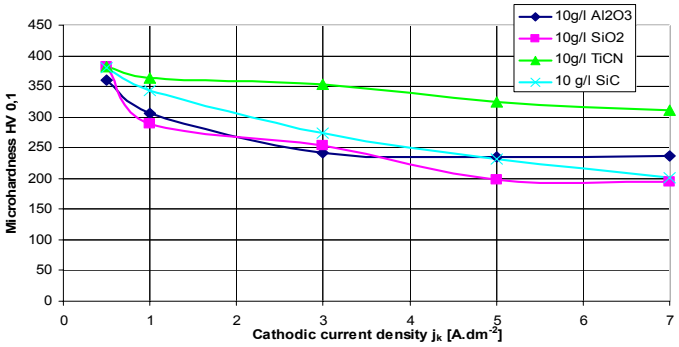

Fig. 9 Dependence of microhardness HV 0,1 on the cathodic current density

4.2 Wear resistance of the coatings

The results of measurements wear resistance of the coatings are presented in Fig. 10 - 12.

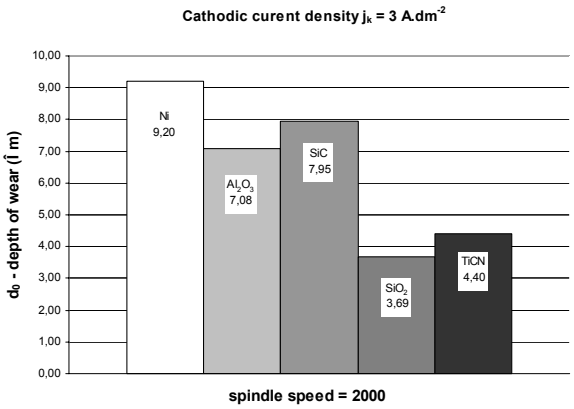

Fig. 10 Adhesive wear resistence of the coatings under investigation after one cycle (after 2000 spindle speed)

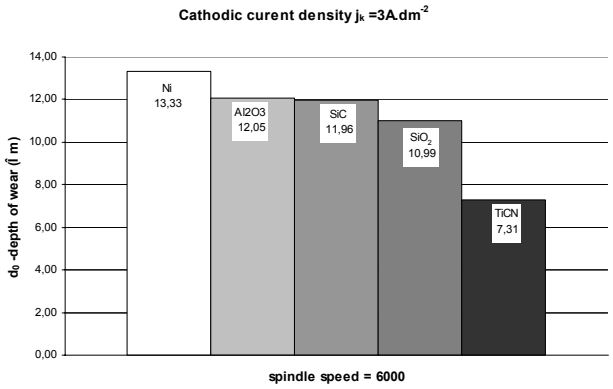

Fig. 11 Adhesive wear resistence of the coatings under investigation after three cycles (after 6000 spindle speed)

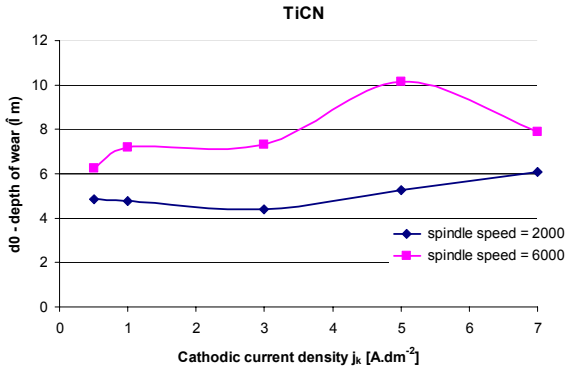

Fig. 12 Dependence of depth of wear on cathodic current density

4.3 Tensile strength

The results of measurements tensile strength are presented in Table 1 and Table 2.

Table 1 Comparision of tensile strength of the coatings: evaluated by punch test and tensile test

Coating / Stearing revolution per minute[min^{-1}]	Tensile strength from punch test [MPa]	Tensile strength from standard tensile test [MPa]
Ni / 200	639	610
Ni / 400	719	724
Ni + SiC / 200	565	561
Ni + SiC / 400	760	741
Ni + Al_2O_3 / 400	1000	910

Table 2 Mechanical properties of the coatings deposited at curent density 3 A.dm^{-2} evaluated by small punch test

Coating	Stearing revolution per minute [min^{-1}]	Tensile strength [MPa]
Ni	200	639
Ni	400	719
Ni+SiC	200	565
Ni+SiC	400	760
Ni+SiO_2	200	650
Ni+SiO_2	400	690
Ni+Al_2O_3	200	950
Ni+Al_2O_3	400	1000
Ni+TiCN	200	1300
Ni+TiCN	400	1600

Mechanical properties evaluation

Mechanical properties, especially tensile strength, of the coatings under investigation were evaluated by small punch test technique. From each coupons (30x30 mm) were cut the punch test specimens . The punch test were performed on INOVA TSM 10 kN servomechanical testing machine at crosshead speed of 0,2 mm/min using disc specimen 8 mm in diameter and about 0,4 to 0,5 mm in thickness. Load versus displacement record was recorded to evaluate maximum force and maximum deflection. From this values tensile strength was calculated using correlation equations developed in Vitkovice – Research and Development, Ltd (Fig. 6). The results are sumarized in table 2. In table 2 the average values of tensile strength from 3 punch tests are presented. In the several CASE the miniaturized tensile test specimen was cut from the electrodeposed coating with the aim to evaluated the tensile strength using standard procedure. The tensile tests were performed on MTS 100 kN servohydraulical testing machine at crosshead speed of 0,5 mm/min. These results are compared with those from punch test in the table 1. From coating with the Al_2O_3 and TiCN particles tensile test specimens could not be manufactured due to excessive hardness values. Even if it was possible to manufactured the tensile test specimen, the tensile strength was affected by microcracks developed in the course of electrospark cutting process. This fact can be seen in table 1. However very good agreement between tensile tests and punch test can be observed, but the further experimental work is

needed to make better recent correlations especially for very hard coatings. From the results presented in table 1 one can conclude a very interesting fact. Tensile strength on electrodeposed composite coatings is a function of dynamical conditions of electroplating process. If the revolutions per minute are increased from the value 200 per minute to 400 per minute the significant change in strength of coating under investigation can be observed . The second interesting fact was identified, some kind of particles increase the hardness of the coating and some kind of particles not. The work is continuing to discuss this phenomenon.

5 CONCLUSION

The following conclusions could be drawn:

1. Nanocomposite coatings were prepared by adding nanometer-sized particles into sulfamate nickel bath.
2. Mechanical properties, especially microhardness and tensile strength of the coatings under investigation were evaluated, tensile strength of the coatings was evaluated by capable small punch test technique developed in Vitkovice-Research and Development, Ltd. There was found a very good agreement between the results of tensile strength evaluated by small punch test and standard tensile test.
3. Adhesive wear resistance of the coatings under investigation were evaluated. It can be seen that the coatings with nanoparticles have much better wear resistance (especially TiCN) compare to the nickel coating.

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